THF Reorientations in THF/D_2O Clathrate

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The SNS site

- The SNS will begin operation in 2006
- At 1.4 MW it will be ~8x ISIS, the world's leading pulsed spallation source
- The peak neutron flux will be ~20-100x ILL
- SNS will be the world's leading facility for neutron scattering
- It will be a short drive from HFIR, a reactor source with a flux comparable to the ILL

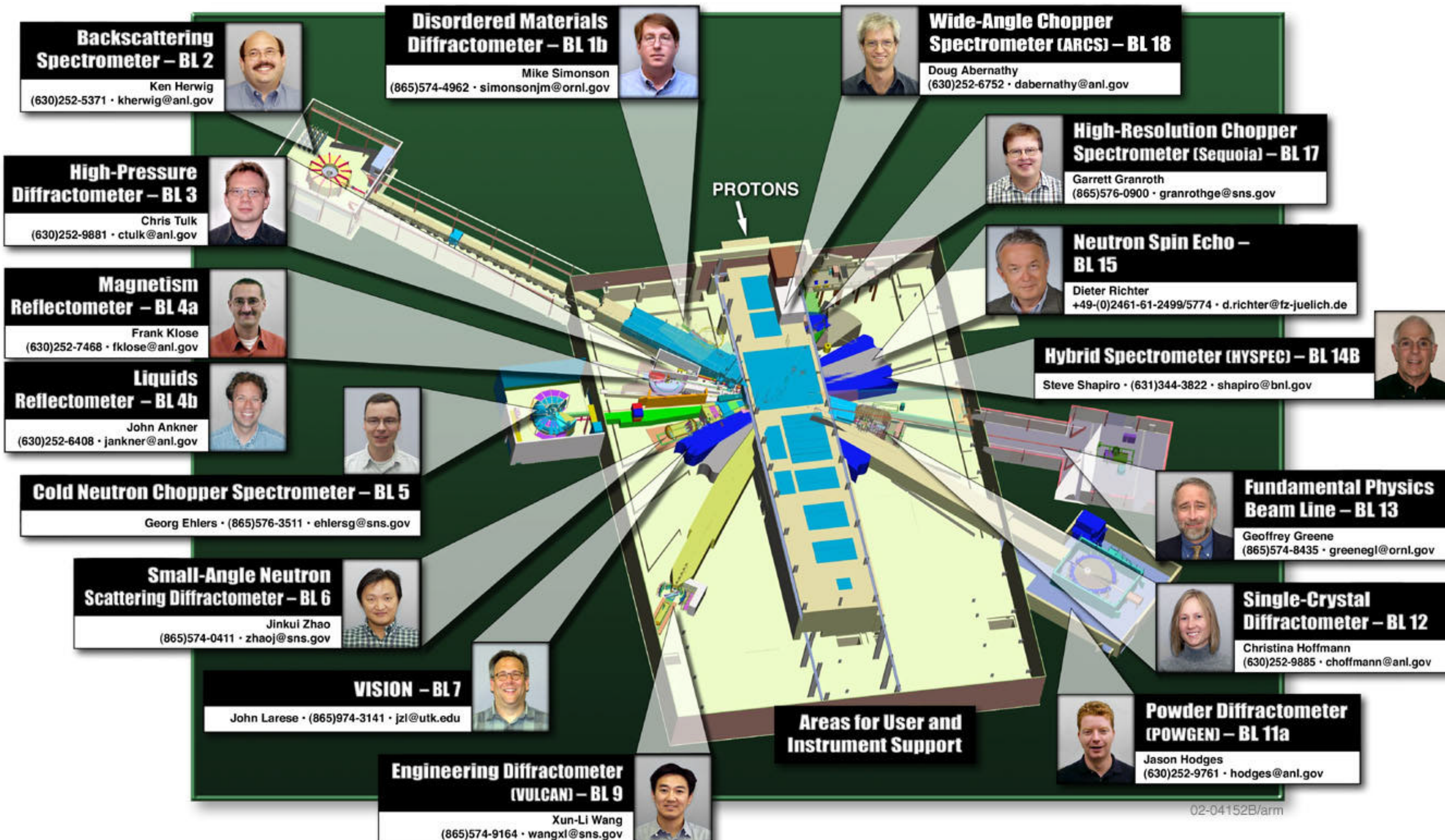
Target/Instruments Buildings

January 2003

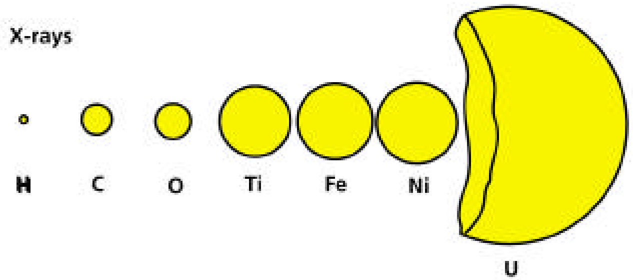
August 5, 2003

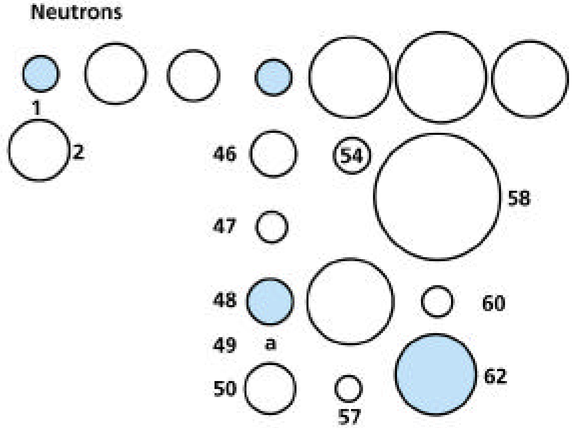
August 2003

Instrument Suite



Why Neutrons?



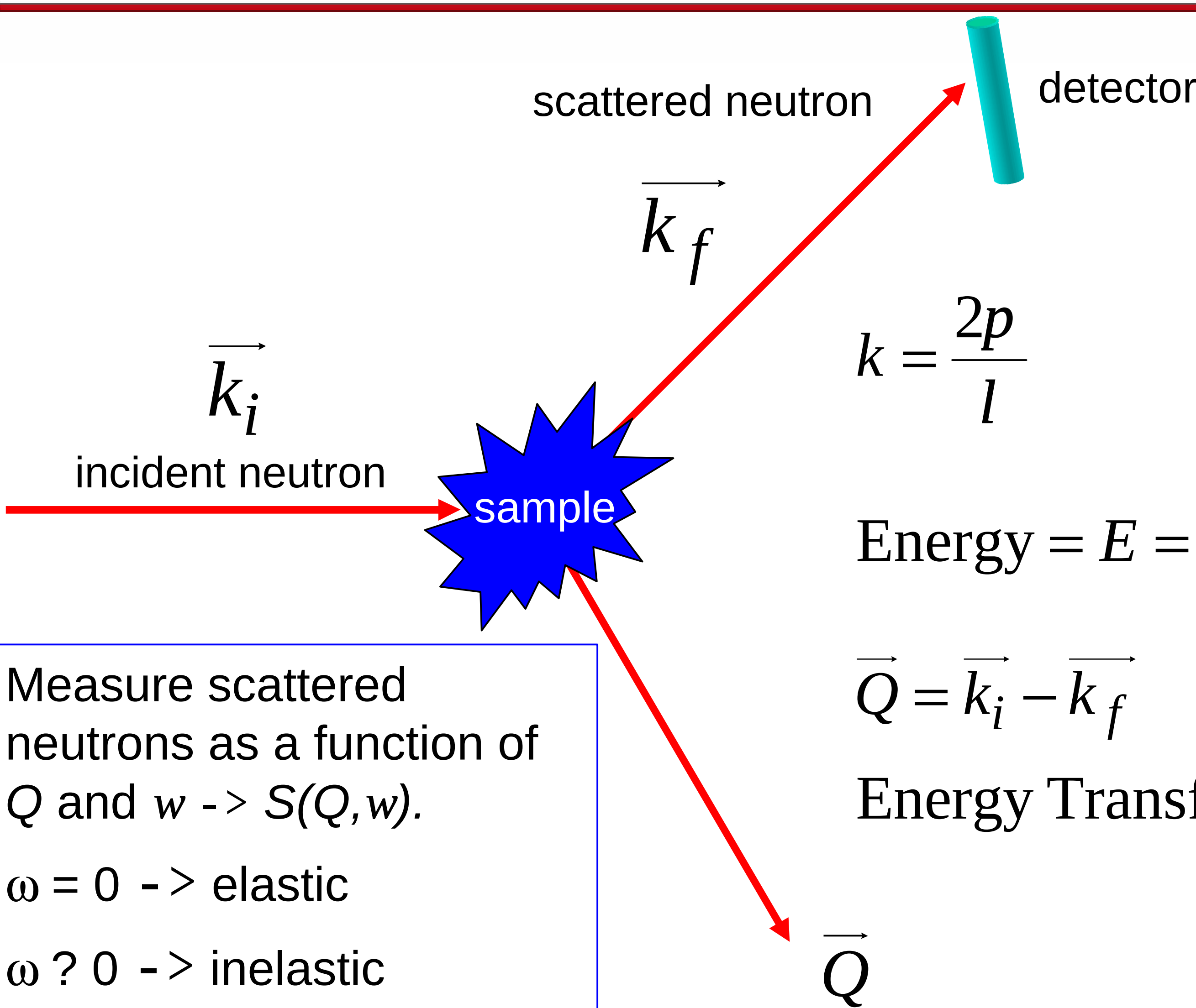


- Isotopic sensitivity – random cross-section with element and isotope
- Wavelength and energy match excitations in condensed matter (Geometry and time):
  - neutrons $\lambda \sim$ Å; E ~ meV
  - x-rays $\lambda \sim$ Å; E ~ keV
  - light $\lambda \sim$ 1000 Å; E ~ eV

1 meV = 11.6 K = 8.01 cm^{-1} = 0.1 kJ/mole = 2.42 x 10^{11} Hz ~ 10^{-12} sec

- Small absorption cross section – can penetrate sample cells
- Weakly interacting probe – sample size implications

Neutron Scattering Experiment



$$k = \frac{2p}{l}$$

$$\text{Energy} = E = \frac{(\hbar k)^2}{2m_n}$$

$$\overrightarrow{Q} = \overrightarrow{k_i} - \overrightarrow{k_f}$$

$$\text{Energy Transfer} = \hbar w = E_i - E_f$$

Measure scattered neutrons as a function of *Q* and w -> *S(Q,w)*.

ω = 0 -> elastic

ω ? 0 -> inelastic

ω near 0 -> quasielastic

Intermediate Scattering Function and *S(Q,w)*

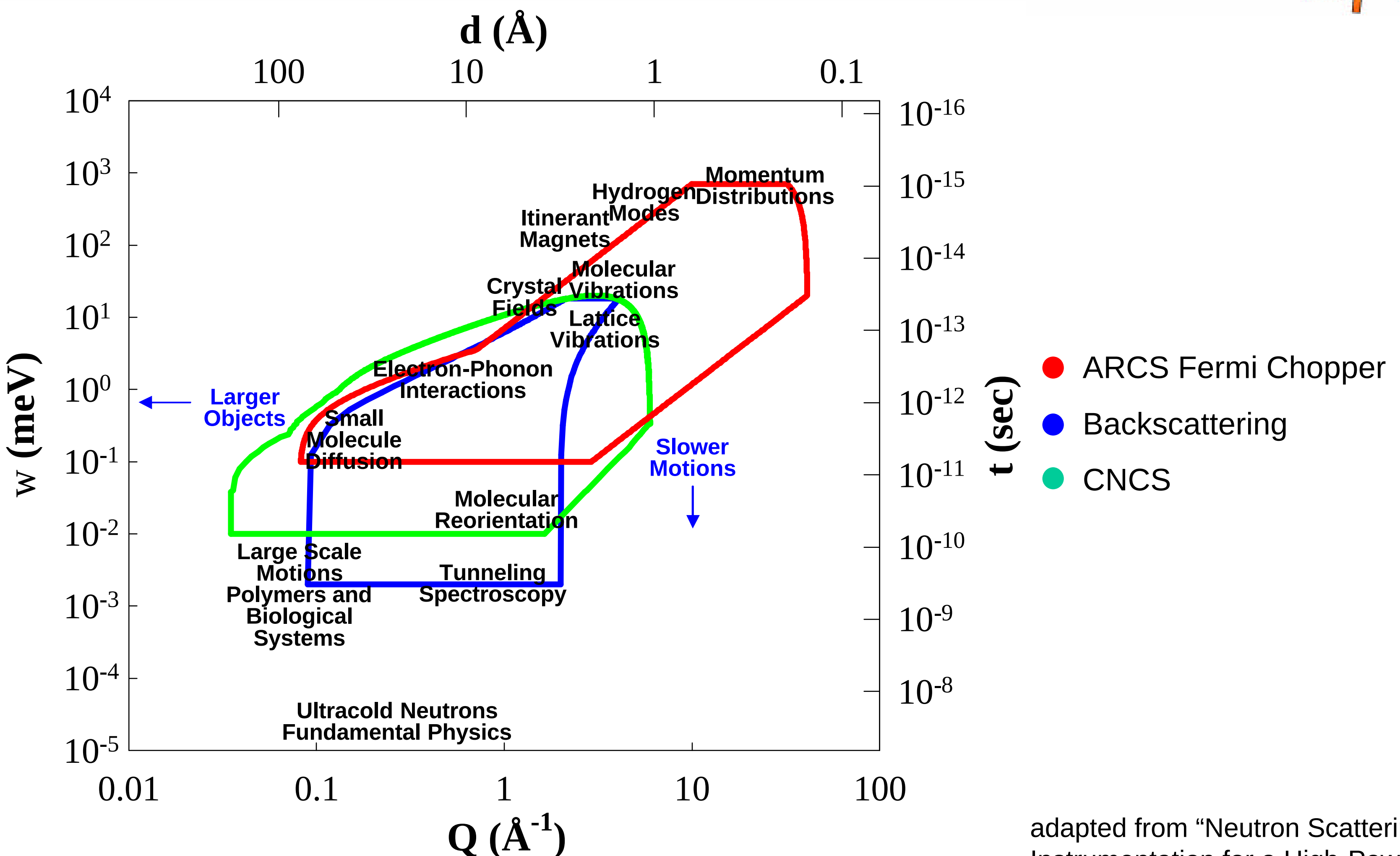
- Intermediate Scattering Function
  - time dependent correlation function
  - incoherent scattering – no pair correlations, self-correlation function
  - calculable from atomic coordinates in a Molecular Dynamics Simulation

$$I_{inc}(\mathbf{Q},t) = \frac{1}{N}\sum_{i}\left\langle \exp\{i\mathbf{Q}\bullet\mathbf{R}_i(t)\}\exp\{-i\mathbf{Q}\bullet\mathbf{R}_i(0)\}\right\rangle$$

- *S_{inc}(Q,w)* – the Fourier transform of *I_{inc}(Q,t)*

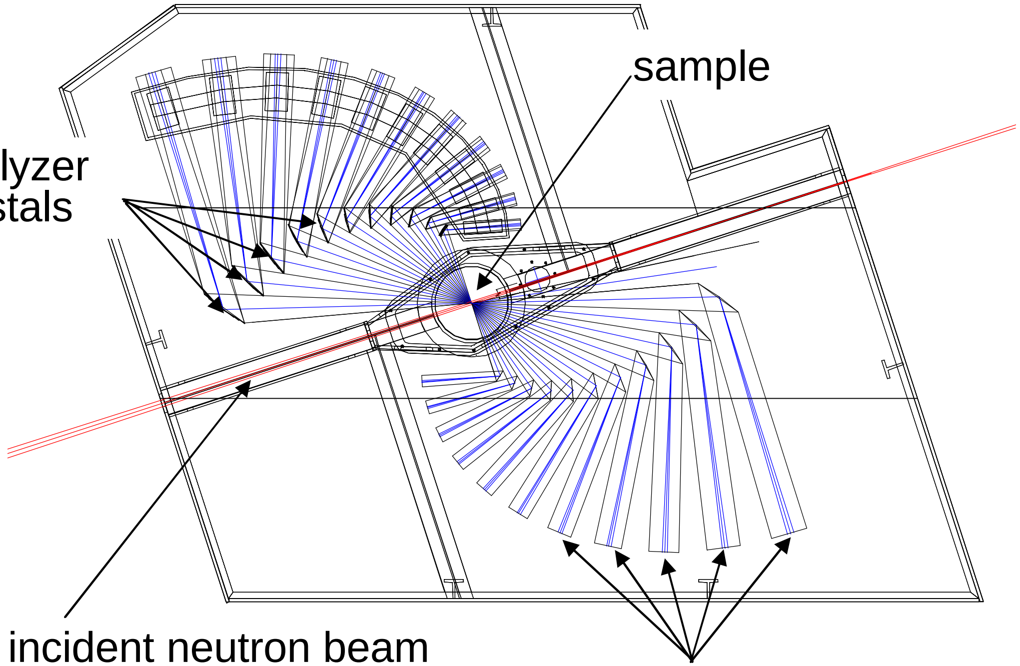
$$S_{inc}(\mathbf{Q},w) = \frac{1}{2p}\int_{-\infty}^{\infty} I_{inc}(\mathbf{Q},t))\exp(-iwt)dt$$

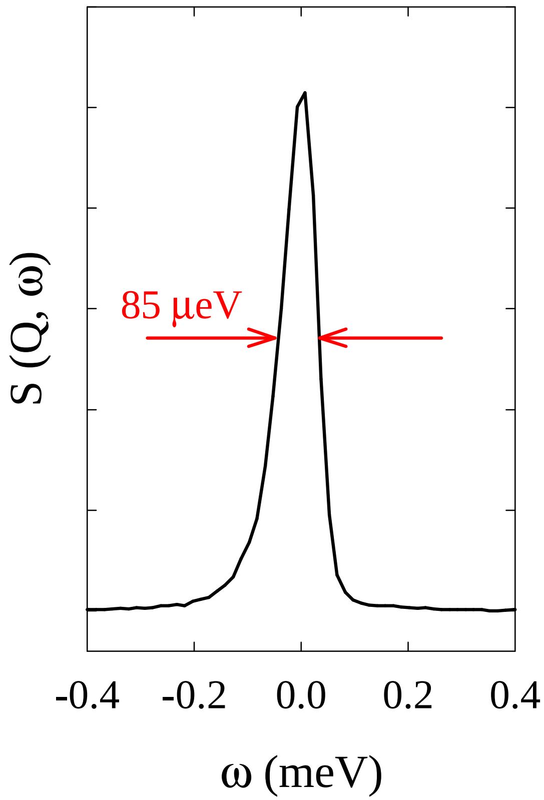
Phase Space probed by Inelastic Instruments



adapted from "Neutron Scattering Instrumentation for a High-Powered Spallation Source" R. Hjelm, et al., LA0-UR 97-1272

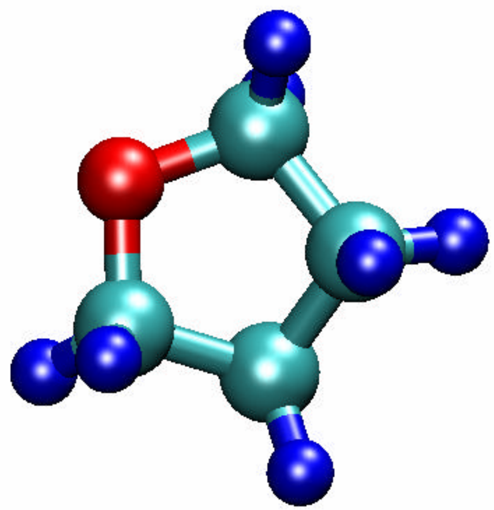
QENS – Intense Pulsed Neutron Source ANL

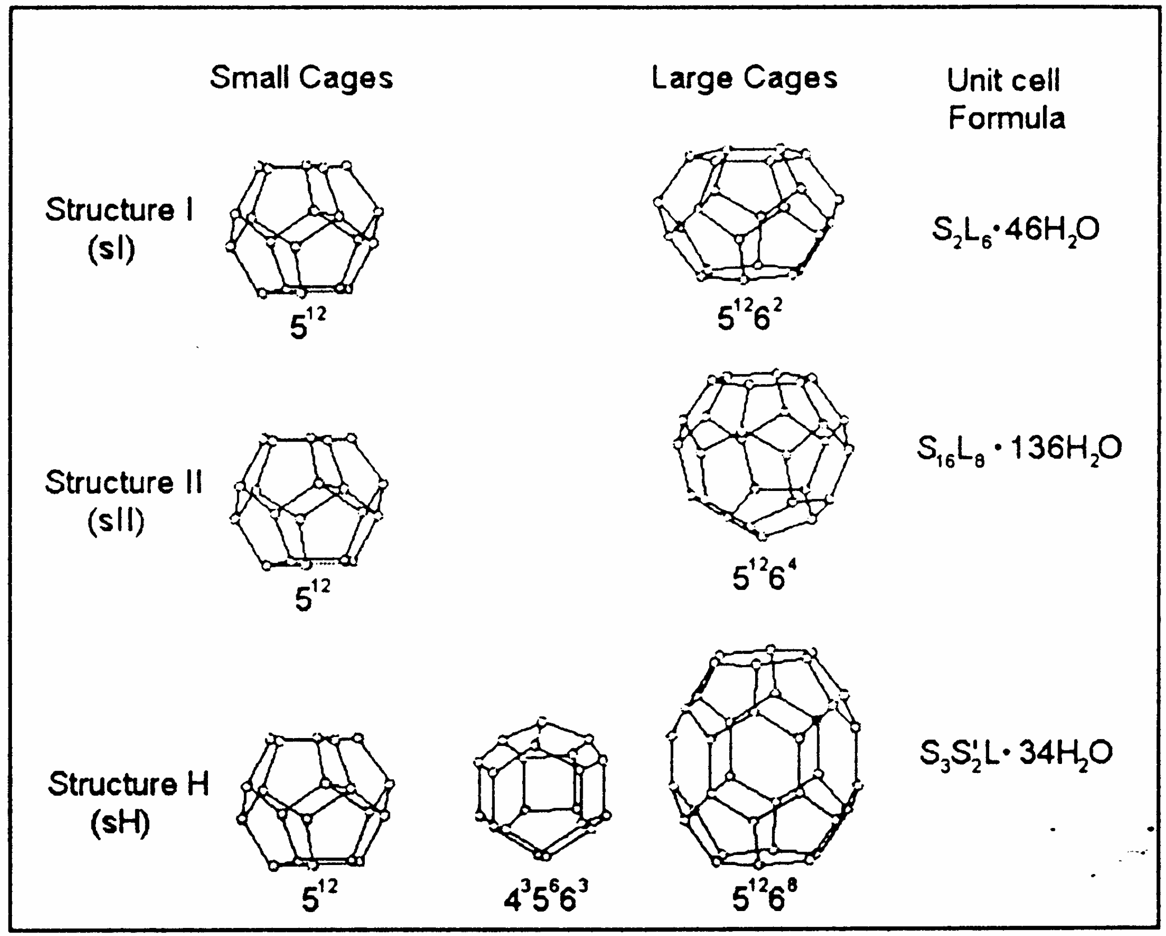




QENS at IPNS, Argonne National Laboratory
time range 1 - 10 psec
$0.36\ \text{Å}^{-1} < Q < 2.53\ \text{Å}^{-1}$

THF (C_4H_8O) Clathrate Hydrate



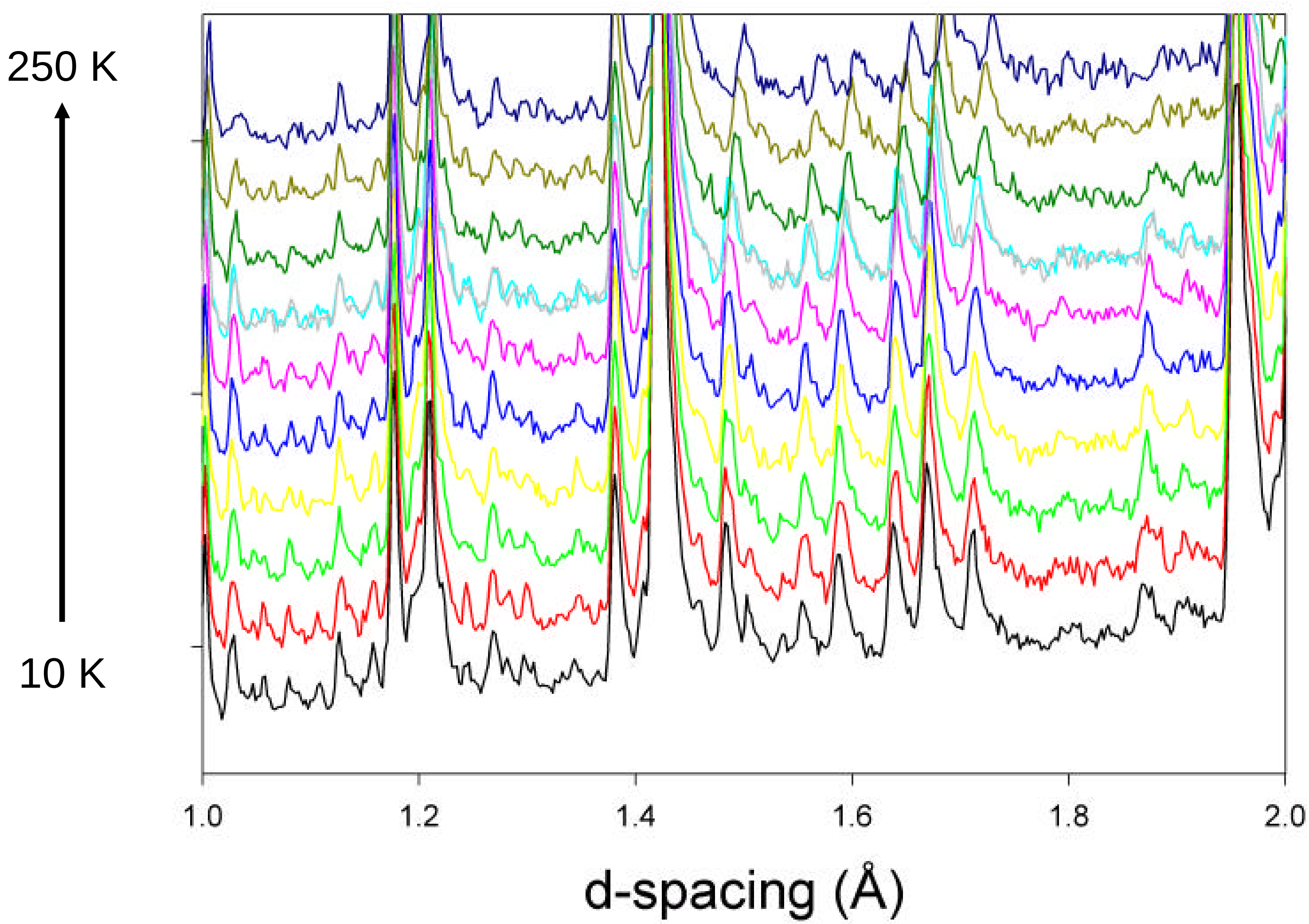


- Structure II
  - Cubic
  - Large Cages 5.9 Å 6.9 Å
  - Avg. radius 4.73 Å
- Melting Temp ~ 277 K

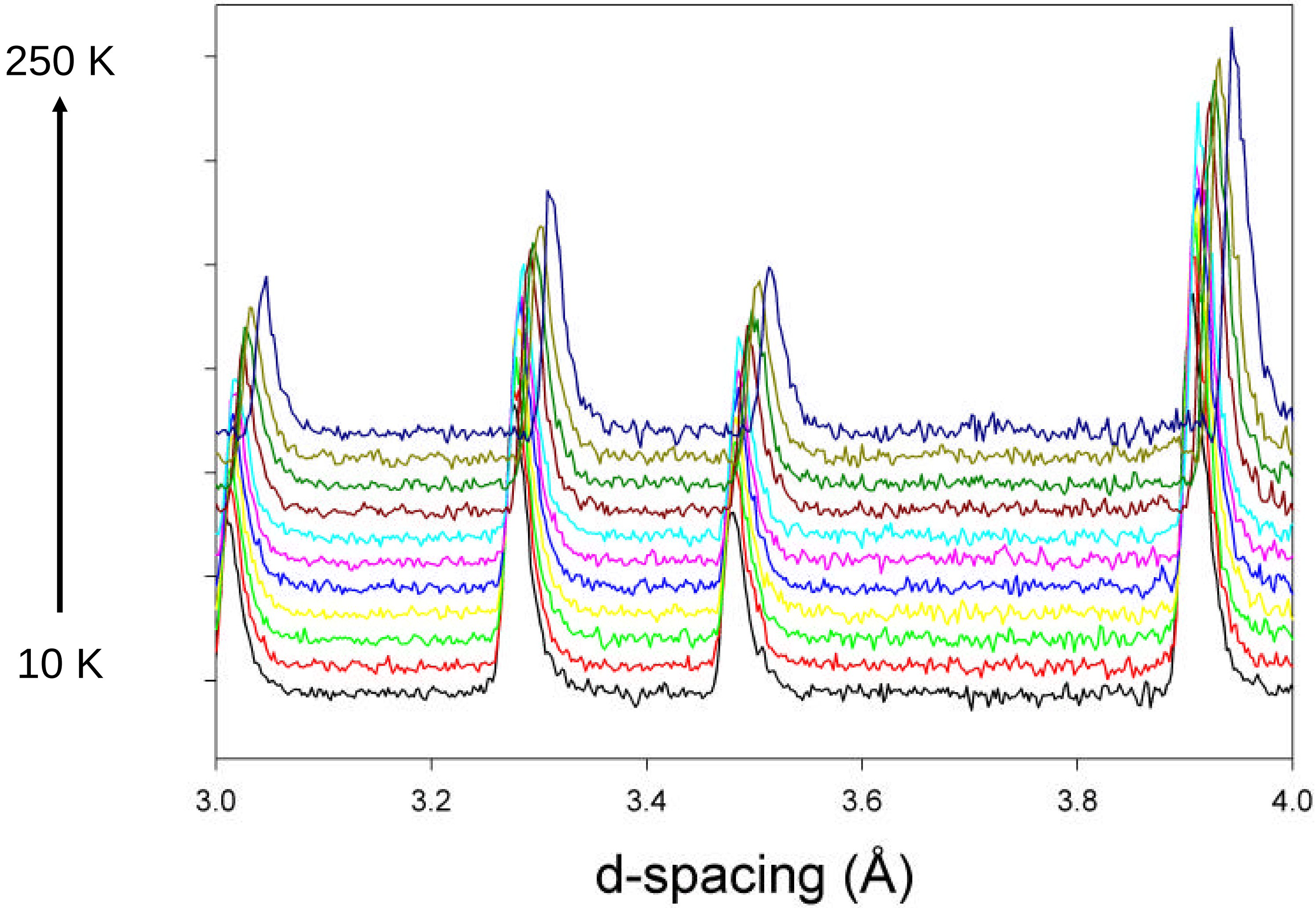
THF Sample Conditions

- Protonated THF (C_4H_8O)
- Deuterated water (D_2O)
- Sample thickness ~ 0.8 mm in beam direction
  - 10% total scatterer (including water) minimize multiple scattering
  - cylindrical annulus 0.4 mm thick, 10 cm tall
- Expect 65% of total scattering from THF H-atoms
- Expect 33% of total scattering from D_2O
  - immobile, elastic with Debye-Waller factor
- 0.017 moles of H-atoms in beam
- 6 hours of beam time

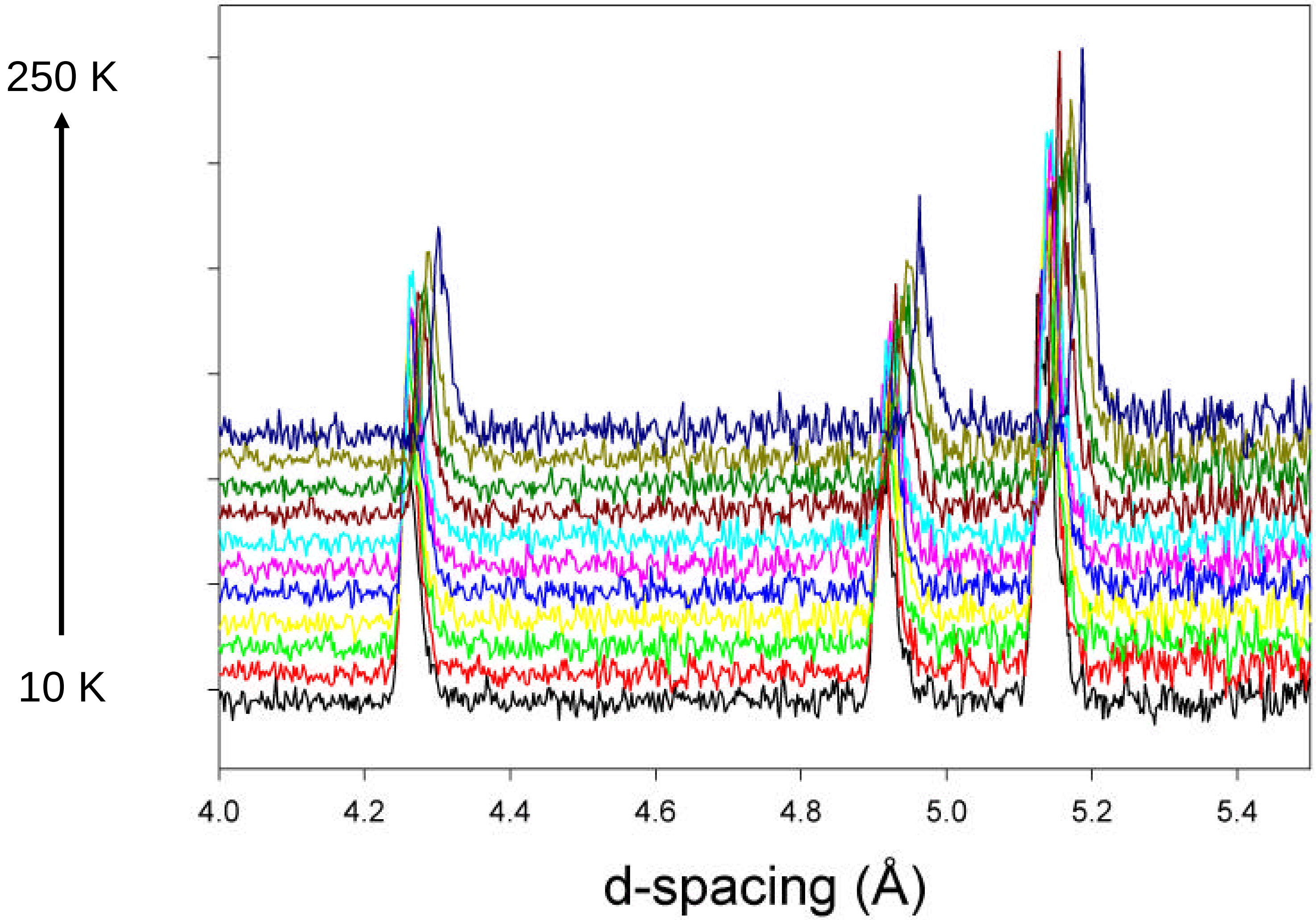
Diffraction Data (h-THF)



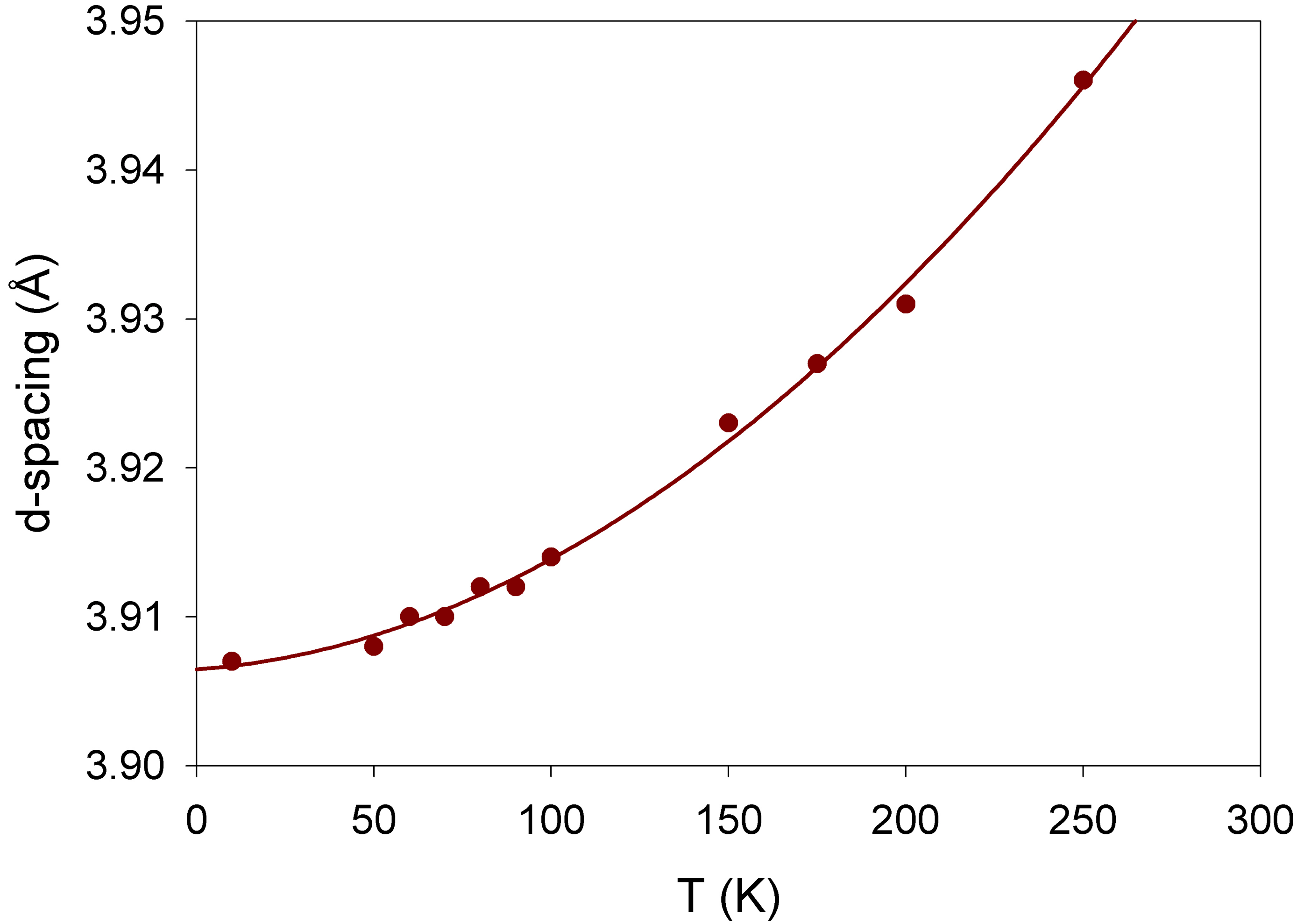
Diffraction



More Diffraction



Lattice Expansion



Quasielastic Neutron Scattering

•Quasielastic Scattering:

•A particle (H-atom) moves out of volume defined by 2p/Q in a time shorter than set by the reciprocal of the instrument sensitivity, dω(meV).

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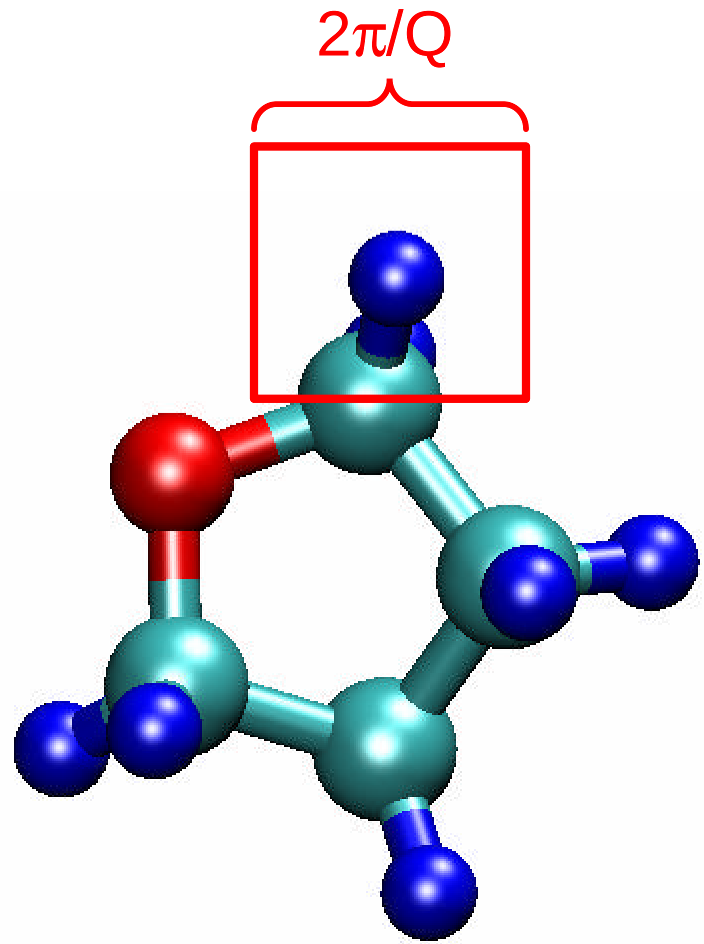
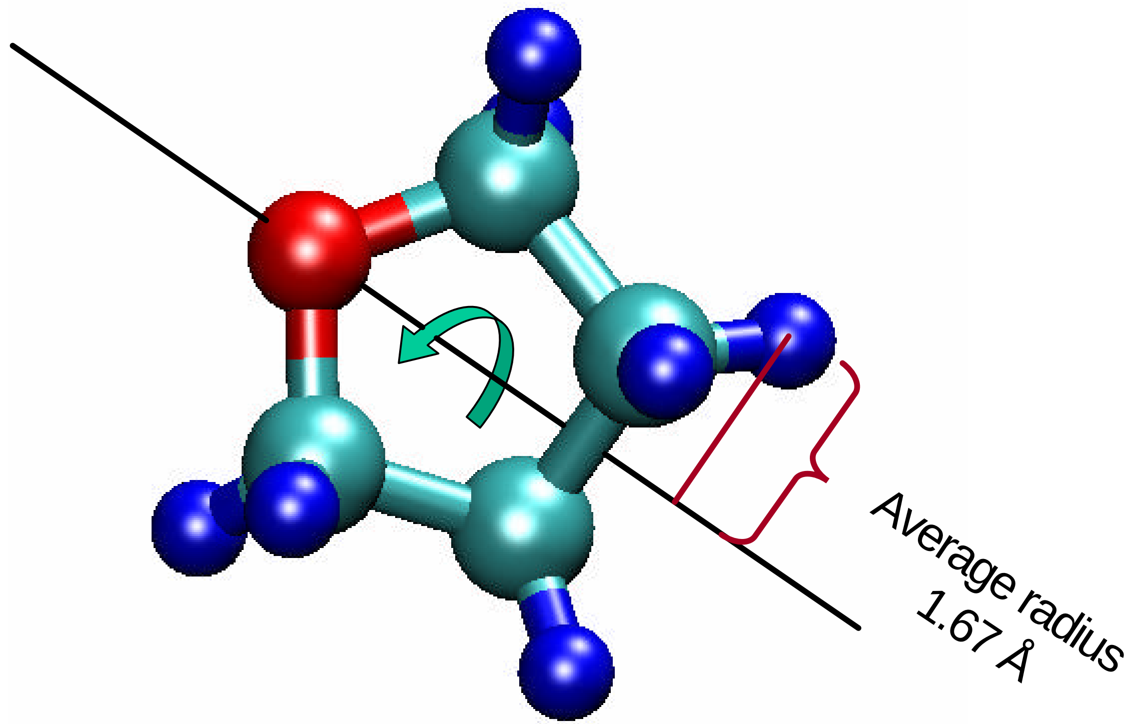
•Isotropic Rotation :

$$t \approx \frac{100\ \ 10^{-12}\,\mathrm{sec}}{dw}$$



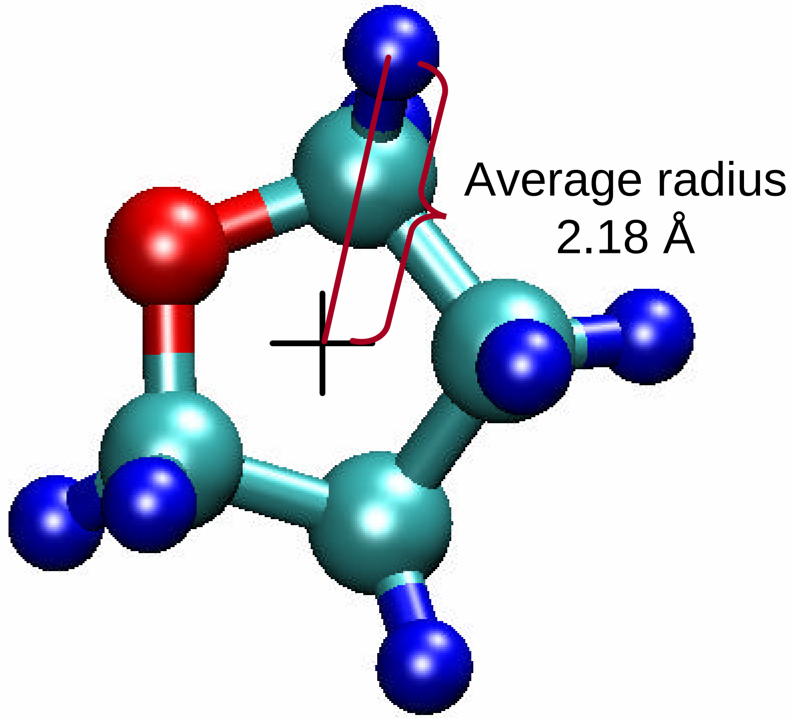
Rotational Models



Uniaxial Rotation (powder avg. of motion in a circle)

$$S(Q,w) = A_0 d(w) + \sum_{l=1}^{N-1} A_l(Q) \frac{1}{p} \frac{t_l}{1+w^2 t_l^2}$$

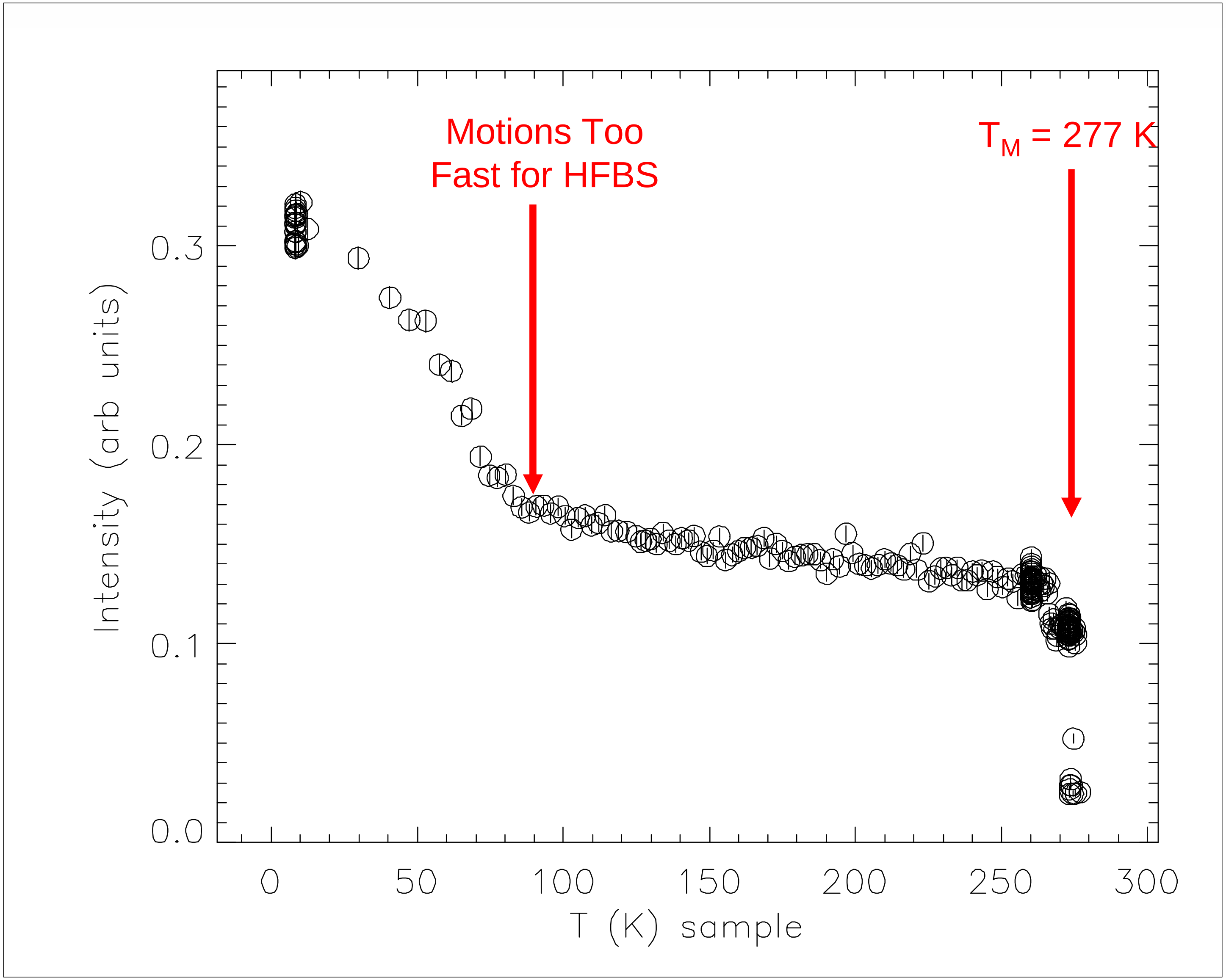
Rotational Models 2



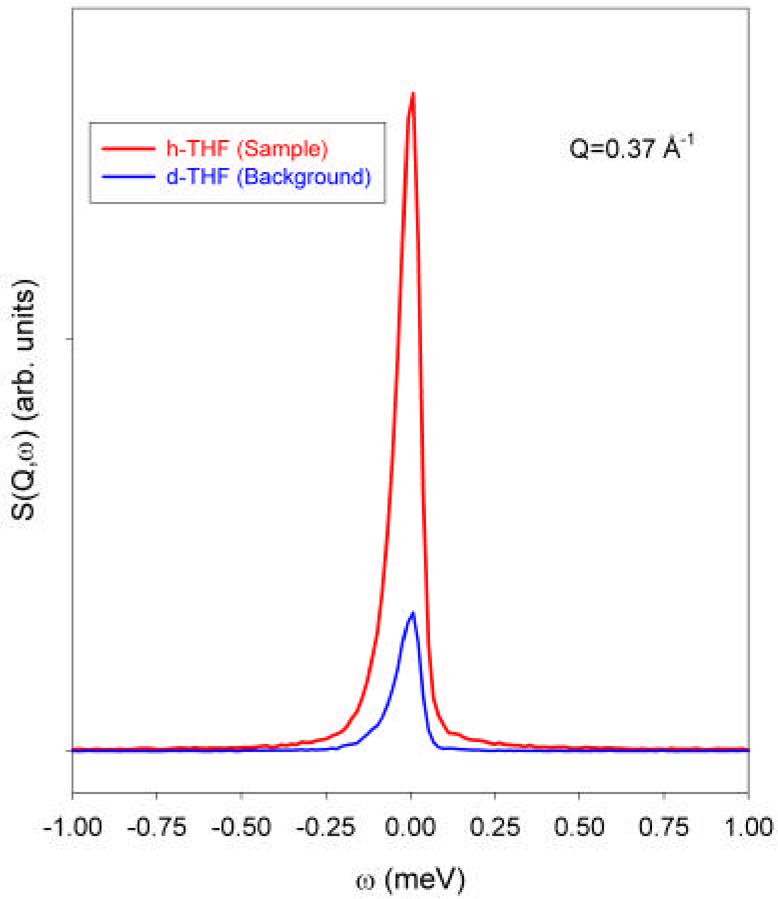
Isotropic Rotation (motion on surface of a sphere)

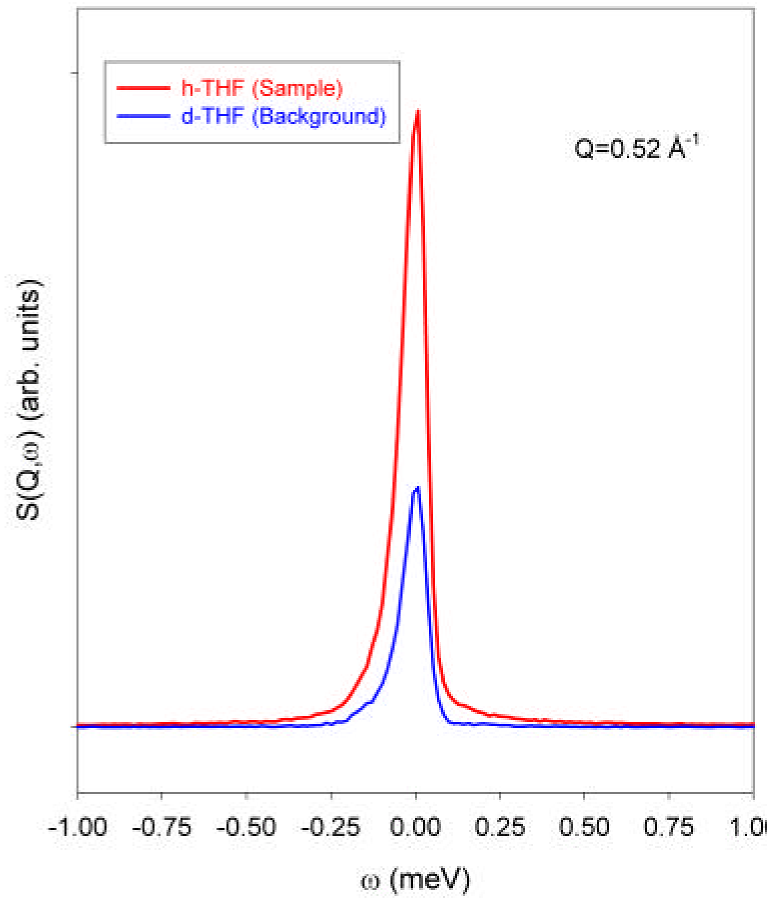
$$S(Q,w) = A_0 d(w) + \sum_{l=1}^{\infty} A_l(Q) \frac{1}{p} \frac{t_l}{1+w^2 t_l^2}$$

Elastic Scan (HFBS – CHRNS at NIST)

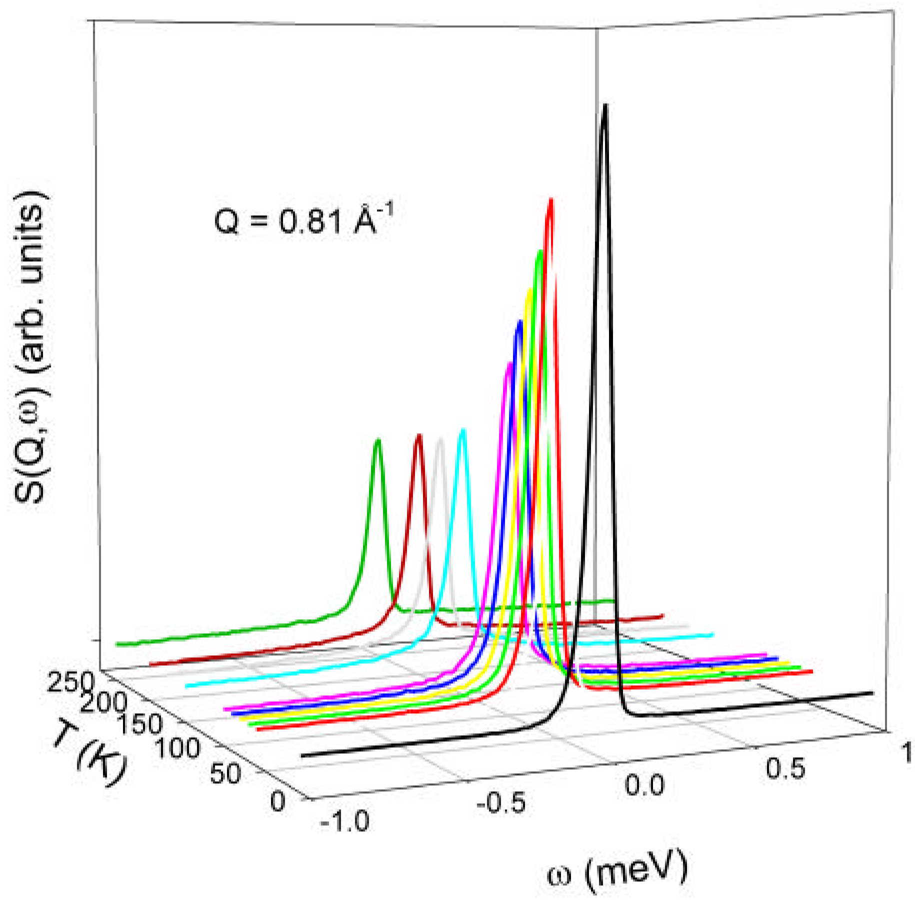


Quasielastic Data/Background 100 K

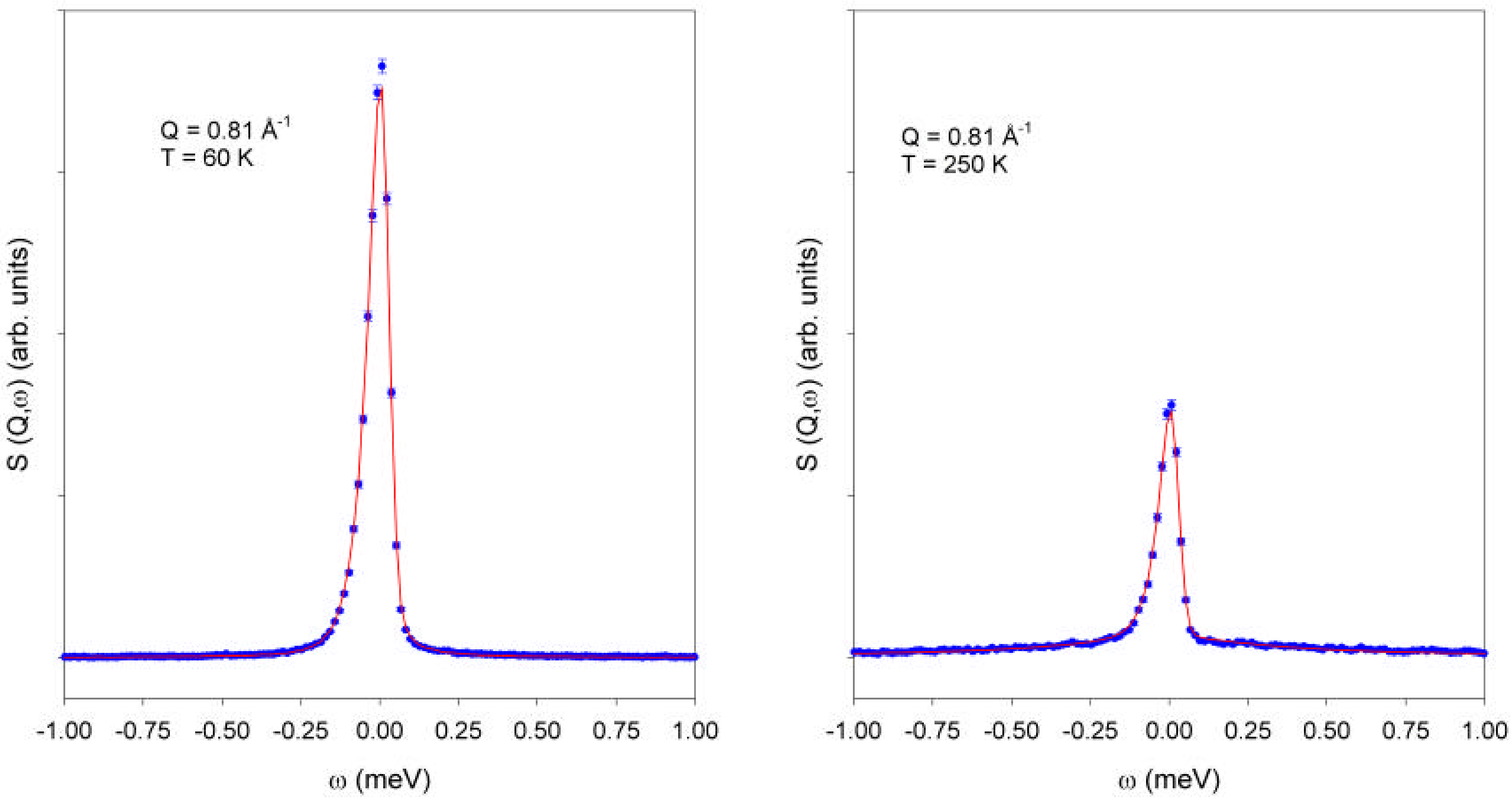




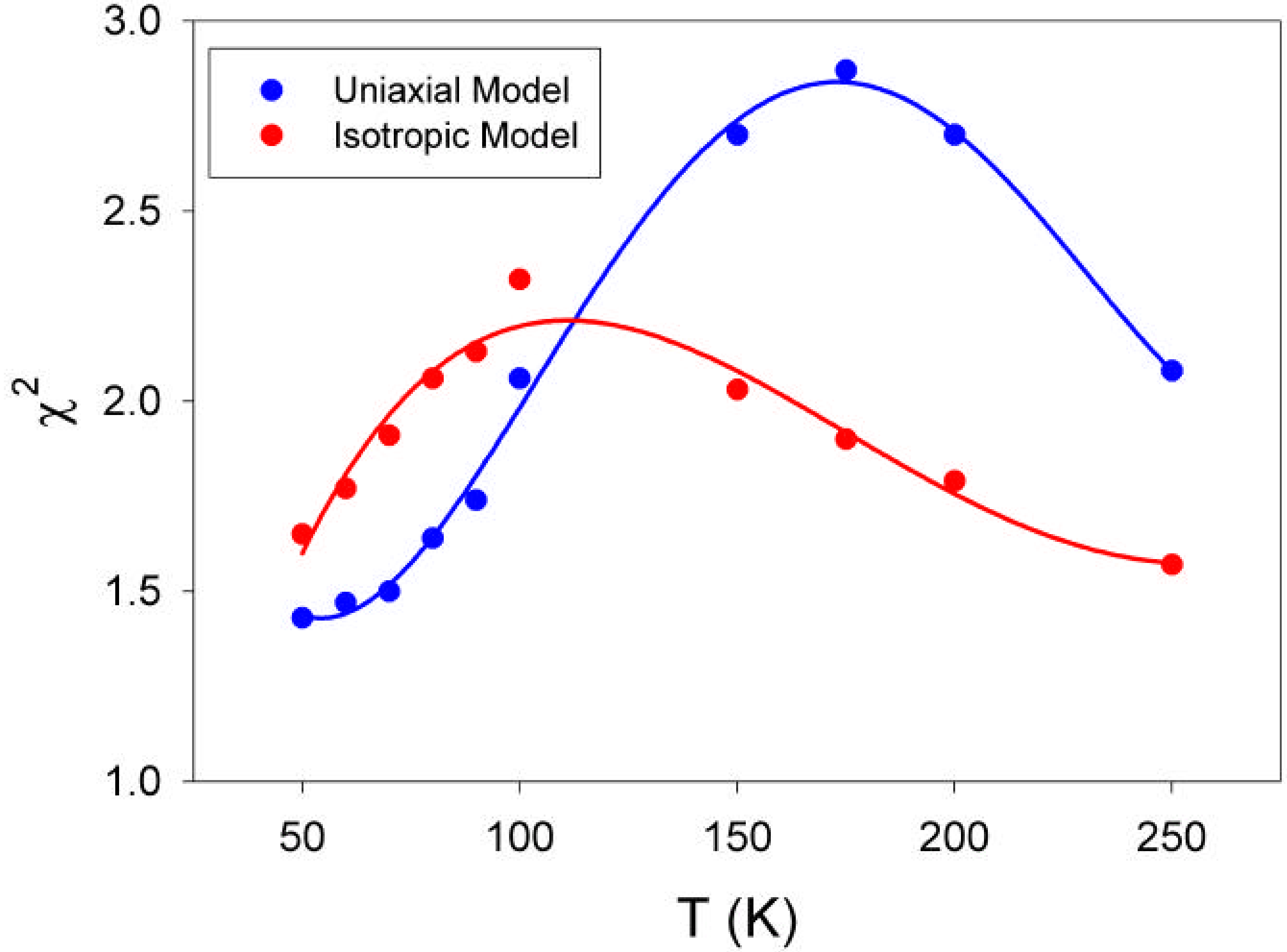
Temperature Evolution Q = 0.81 Å^{-1}



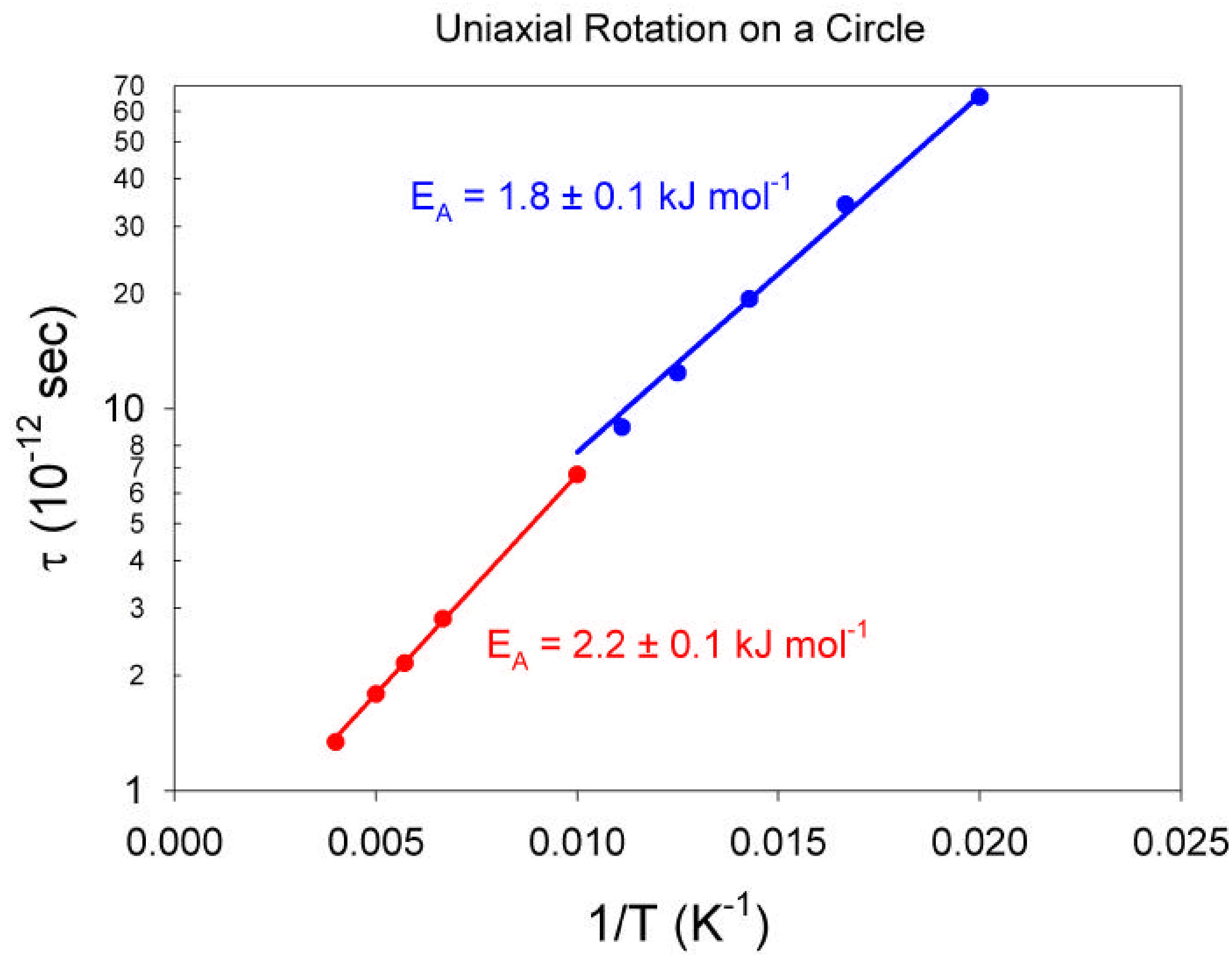
Model Fits to Data



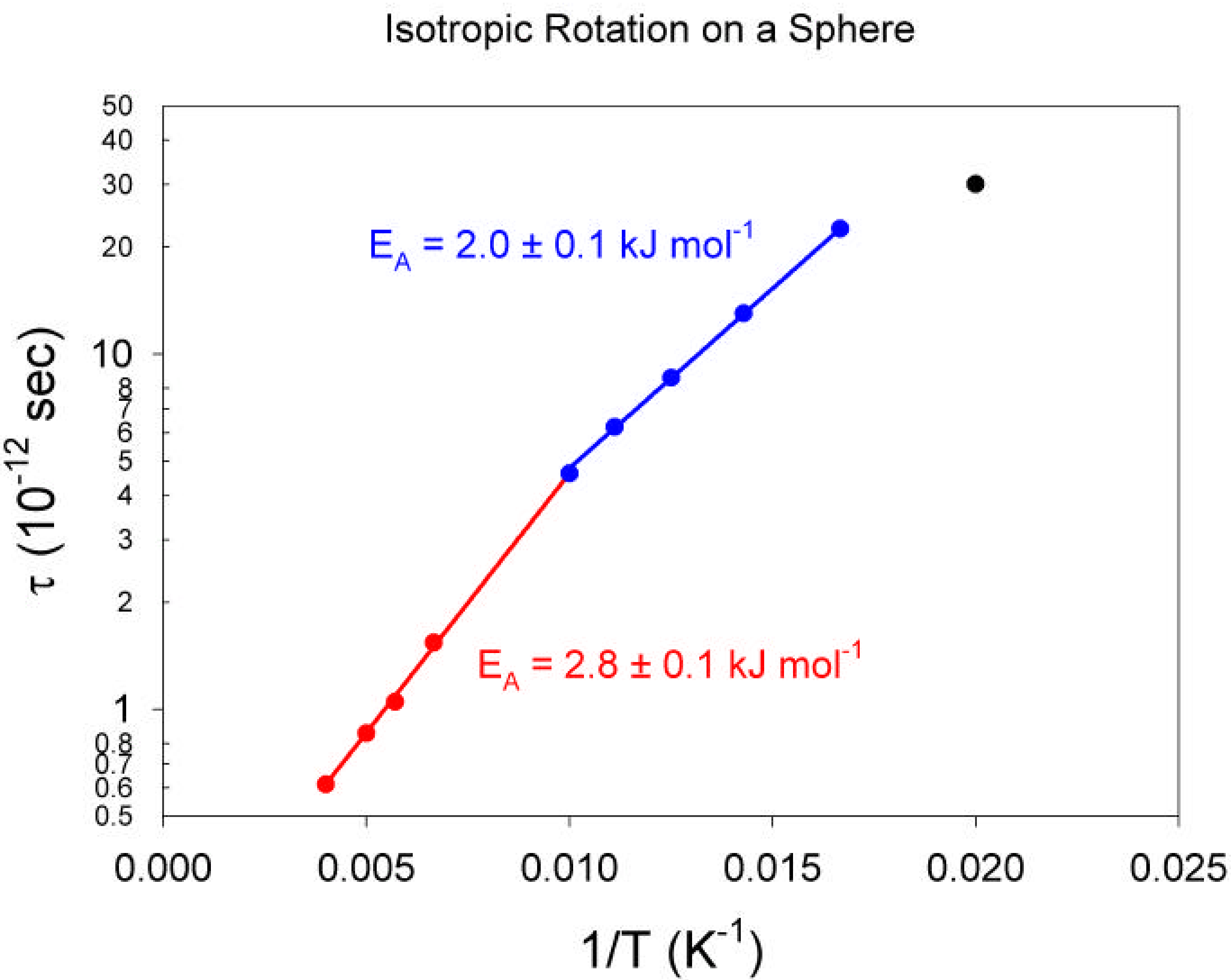
Compare the two Quasielastic models: χ^2



Uniaxial Model



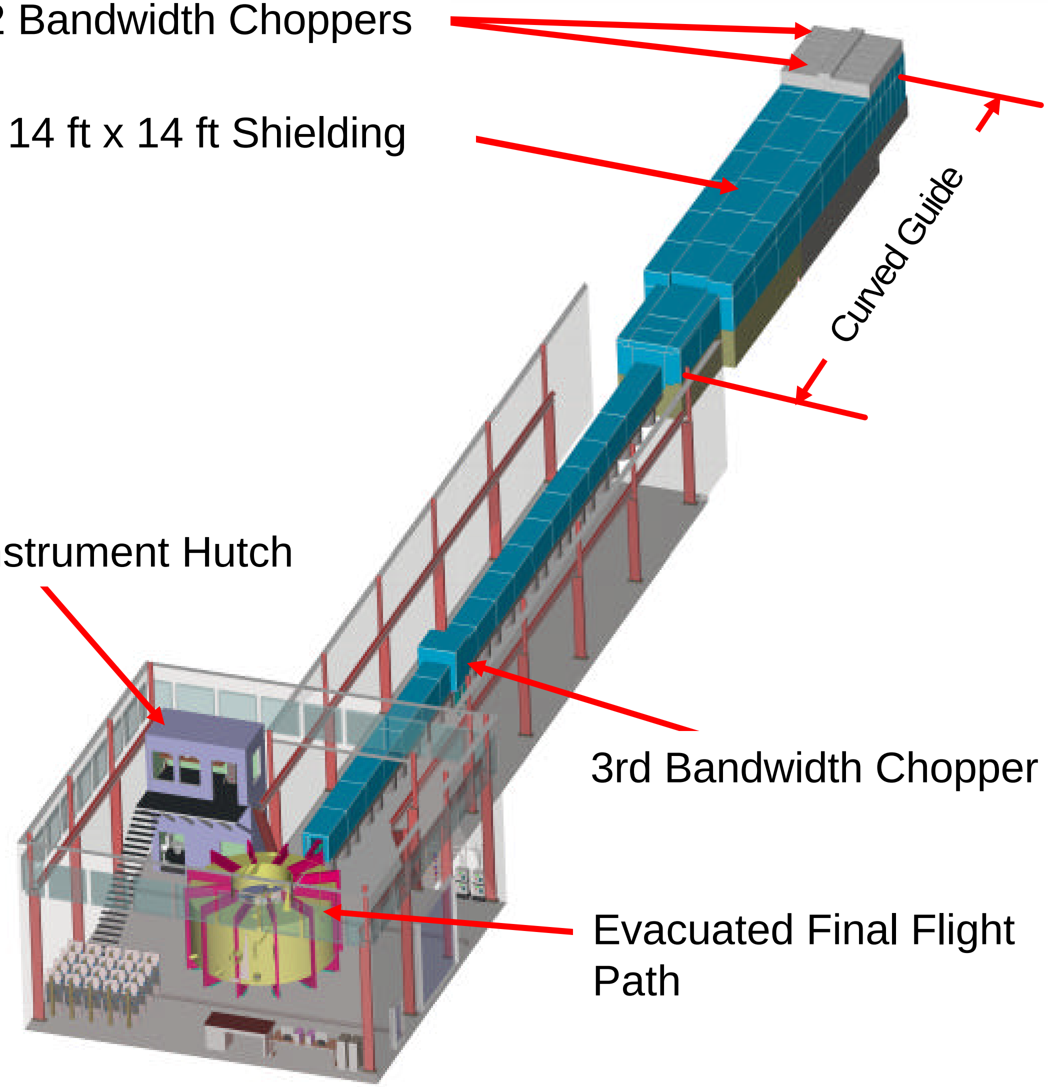
Isotropic Model



CONCLUSION

- Web sites for the Spallation Neutron Source
  - www.sns.anl.gov – Instruments only
  - www.sns.gov – project public site
    - Follow links to user information and to instrument data sheets www.sns.gov/users/instrument_data_sheets.pdf
- THF
  - Two clearly identified regions: < 100K, 100 K – 250 K
  - Geometry of motion at T < 100 K more restricted than at higher T
  - In both T regimes, activated dynamics
    - – isotropic (sphere) high-T: 2.8 ± 0.1 kJ mol^{-1}
  - Future Work
    - Refine Diffraction Data
    - More sophisticated rotational models
      - Whole molecule rotations about fixed and mobile axes

Instrument View
Backscattering Spectrometer Beamline 2TU



- 84 m incident flight path
- Si (111) analyzer crystals
- Elastic Resolution 2.7 μeV
- Dynamic Range ± 260 μeV
- $0.1\ \text{Å}^{-1} < Q < 2.0\ \text{Å}^{-1}$
- $-0.3\ \text{meV} < \omega < 18\ \text{meV}$
- Up to 100x performance of current instruments

Final Flight Path